

CHAPTER 16

Hydrated Calcium Silicate Products Other Than Hydraulic Cements

G. E. BESSEY

*The Chalk Lime and Allied Industries Research Association,
Welwyn, Hertfordshire, England*

CONTENTS

I. Introduction	101
II. Calcium Silicate Bonded (Sand-lime) Bricks	102
A. The Factors Affecting Quality of Calcium Silicate Bonded Bricks	107
B. The Constitution and Microstructure of Calcium Silicate Bricks	113
C. The Relation between Composition of the Bonding Material and the Technical Properties of the Product	119
III. Aerated (Foamed) Calcium Silicate Products	121
A. Properties	122
B. Structure and Constitution	124
IV. Calcium Silicate Bonded Asbestos Products	125
V. Very High Strength Calcium Silicate Bonded Products	126
VI. Calcium Silicate Fillers	126
A. Manufacture	128
B. Chemical Composition and Constitution	128
C. Particle Size, Surface Area, and State of Aggregation	129
VII. Lime-stabilized Soils	130
References	131
Addendum	133

I. Introduction

The conscious industrial utilization, by direct synthesis, of hydrated calcium silicates is nearly as recent as the understanding of their nature and properties. The industrial developments have so far, for the most part, been along empirical lines completely independent of the fundamental chemical and physical investigations. With the increasing knowledge of these compounds, and wider understanding of the manner

in which the effects of conditions of manufacture determine the particular calcium silicate produced, there is potential of wider utilization.

The hydrated calcium silicate now being formed by mankind each year amounts to some hundreds of millions of tons. Indeed, with the possible exception of the anhydrous aluminosilicates, formed in clay bricks and other ceramic products, the amount of tobermorite and related phases made exceeds that of any other chemical compound. The greater part of this large annual production is formed in concrete and mortars in the setting and hardening of Portland and other hydraulic cements dealt with in other chapters. Apart from this, however, very considerable amounts are made by direct synthesis in the following ways.

- (a) Production of calcium silicate bonded building units, including sand-lime bricks, flint-lime bricks, lime-based aerated concretes, building boards and the like, all hardened by hydrothermal synthesis of the silicate from lime and silica.
- (b) Production of calcium silicate bonded thermal insulating materials, using hydrothermal synthesis.
- (c) Production, generally by precipitation, of finely divided calcium silicate fillers.
- (d) Formation as a product of the lime-clay reaction, in the use of lime for soil stabilization in road construction.

These processes, the technical properties and qualities of the products formed and the relation of these properties to the chemistry and constitution of the hydrated calcium silicates themselves, so far as is at present known, will be considered in this chapter.

II. Calcium Silicate Bonded (Sand-lime) Bricks

Bricks composed of sand and lime, hardened by curing in high-pressure steam, with formation of a hydrated calcium silicate bond, were first made commercially in Germany about 1898, although patents covering such a process were taken out by Van Derburgh in England in 1866 [1] and by Michaelis in Germany in 1880 [2]. The English term "sand-lime brick", applied to these products before the nature of the hardening process was known, is somewhat misleading and is now being slowly replaced in the industry by the term "calcium silicate brick". This term has the advantage of including a wider range of products of the same class now being made, where siliceous materials other than sand are used. The German term "Kalksandstein" and the French "briques silico-calcaire" are both clearly descriptive.

The growth in production of calcium silicate bricks has varied very

widely from
The relative
making of
concrete
has also be
stone bloc
brick; are
the aerate

Year

1800
1910
1927
1930
1933
1934
1935
1940
1950
1958
1960

a) y
a) x

Table
available
and othe
a domin
internal
lar th
fac b
bricks a
facings e
at relati
and shal
The calc
size but

widely from one country to another, depending upon a number of factors. The relative availability of suitable sand, of suitable clay for clay brick-making and of gravel or stone or by-products from industry for use as concrete aggregate, has been the dominant factor. Tradition in building has also been significant in its effects; areas where the tradition has been stone block construction have more readily adopted concrete block than brick; areas where timber has been traditional have more readily adopted the aerated concretes, to obtain the equivalent insulation.

TABLE I

The annual production of calcium silicate (sand-lime) bricks (millions)

Year	United Kingdom	Germany	Holland	U.S.A.	U.S.S.R.
1900	—	300	—	—	—
1910	—	1600	120	—	—
1927	—	—	—	320	—
1930	100	1600	—	191	—
1933	—	—	600	—	—
1934	—	—	—	11	—
1935	108	—	—	—	—
1940	200	2800	—	—	—
1950	123	1000 ⁽¹⁾	—	—	—
1956	132	—	—	—	—
1960	223	3290 ⁽¹⁾	1000	(2)	6000

⁽¹⁾ W. Germany only.

⁽²⁾ No figures available, but believed to be less than 50.

Table I shows the production in some countries for which figures are available. In parts of Germany, where suitable sand is widely available and other raw materials are not, calcium silicate bricks have achieved a dominant position among structural building materials, both for internal and external work. In Holland, also, the production is very large; there, however, clays from which attractive and good quality facing bricks can be made are also available and the calcium silicate bricks are used almost entirely for backing or internal work, with clay facings externally. In Great Britain common clay bricks can be produced at relatively low cost because of the availability of carbonaceous clays and shales containing part of the fuel necessary for burning the bricks. The calcium silicate brick industry has therefore not grown rapidly in size but has been forced to concentrate upon the better quality products

for facing work and other special uses. It has therefore probably given greater attention to research into the factors affecting quality than the industry has in most other countries.

In parts of the U.S.S.R. the position has been similar to that in Germany, with wide availability of suitable sands, and this class of brick is now used in great quantities; few figures of production are available, however. In the United States of America, on the other hand, the sand-lime brick is now little used. Production reached a peak in the 1920-30 period at about 320 million bricks a year but has since receded to a very low current figure with the continued growth in use of concrete block; clay brick production has receded similarly. In other countries production is at present relatively small but there is a growing potential in some of the less well developed countries.

The description given in the following pages of the properties of calcium silicate bricks and the important factors in their manufacture, is necessarily brief. More detail on some of these matters and information regarding the use of this class of brick has been given elsewhere by the present author [3].

The more important properties of building bricks or blocks are listed in Table II, with an indication of the commercial range for calcium silicate bricks, compared with the ranges for clay bricks, and for lightweight concrete and dense concrete bricks or blocks. It is apparent from this table that in general the calcium silicate bonded material compares favourably with the competitive products, although inevitably each material has its relative advantages and disadvantages.

It is clear from this table that, when properly utilized, the strength of the calcium silicate bond formed by hydrothermal reaction of lime and silica can be as effective as that derived from the hydration of Portland cement or from high-temperature ceramic bonding. The influence of the various factors in manufacture upon the effectiveness of bond and thus upon strength development is considered later. The knowledge of such factors makes it possible to produce material of any required strength within the range given in Table II. Manufacturers having such knowledge, therefore, frequently make a number of closely controlled grades of brick of specified compressive strength, in steps of 1000 lb/in², e.g. 2000, 3000, 4000 and 5000 lb/in²; † from these the grade most suitable for a given job can be chosen. The close control of strength enables the architect to design buildings with minimum wall thicknesses without fear that some of the bricks used may be appreciably below the strength on which he has based his design.

Most materials shrink slightly when dried and expand when wetted.

† Strengths in this chapter are given in lb/in²; 1 lb/in² = 0.070307 kg/cm².

The drying
are usually
during prod
building. Th
being zero i

The

Prope

Strength
Compressive
(lb/in²) tested
condition

Volume %
Drying shrink
cent of length

Thermal conc
(B.t.u. ft⁻² h
deg F⁻¹)

Durability us
natural expor

Fire resistan

Properties of
laying and p

Liability to e
(soluble salts)

Density (lb/

* Clay b.
particularly
† Accord
‡ Aerate
value withi

4*

The drying shrinkage is one cause of cracking in buildings, since materials are usually wet when the building is erected and ultimately dry out during prolonged warm dry weather and as a result of heating of the building. The drying shrinkage of building materials varies very widely, being zero in metals and glass and a maximum with organic materials.

TABLE II

The normal range of properties of building bricks and blocks

Property	Calcium silicate bricks	Clay bricks	Concrete bricks (dense)	Aerated concrete block (auto-claved)	Light-weight aggregate concrete block
<i>Strength</i>					
Compressive strength (lb/in ²) tested in a wet condition	1500-8000	1500-12000	1000-5000	300-800	300-2500
<i>Volume stability</i>					
Drying shrinkage (per cent of length)	0.01-0.035	0.00-0.015*	0.02-0.05	0.05-0.10	0.04-0.08
<i>Thermal conductivity (k)</i> (B.t.u. ft ⁻² hr ⁻¹ in ⁻¹ deg F ⁻¹)	8-11	5-9	7-12	0.7-1.5	1.0-5.0
<i>Durability under severe natural exposure</i>	Good if strength above 2000 lb/in ²	Excellent to very poor†	Good to poor†	Good	Good to poor†
<i>Fire resistance</i>	Good	Very good to moderate†	Good to poor†	Very good	Very good to poor†
<i>Properties affecting laying and plastering</i>	Good	Varied; good to poor†	Good	Good	Good
<i>Liability to efflorescence (soluble salts)</i>	None	Very from none to severe; † fairly common	None or slight†	None or slight†	Generally none
<i>Density (lb/ft³)</i>	105-130	90-150	110-140	25-55‡	40-100

* Clay bricks have sometimes a small but significant progressive expansion, more particularly during their early life.

† According to quality and type.

‡ Aerated concretes are normally made to a closely controlled density at a specified value within this range. The most widely made grades have densities of 45-60 lb/in³.

Timber shrinkage may be as high as 7% across the grain, although only up to 0.2% along the grain. The figures for the various materials shown in Table II seem small compared with this; they are nonetheless significant in brittle structures where there is little elastic movement. Calcium silicate bricks have drying shrinkages below the values obtained with concrete products but generally higher than those normally found with burnt clay products. It is therefore important in manufacture to keep the drying shrinkage as low as possible, and in use to design the building and utilize techniques of construction so that stresses arising from any shrinkage are minimized.

Thermal conductivity of a building material [4] is of primary importance as affecting heat losses and thus heating costs. Generally, it is a function of the bulk density of the unit and the chemical nature of the constituents have relatively little influence upon the value. A material which is essentially of crystalline structure tends to have a slightly higher conductivity than one that is partly glassy, so that sand-lime bricks have slightly higher conductivity than clay bricks of the same density; the difference is not, however, sufficient to be of any practical significance.

While it is obvious that building materials must have good durability, it is not at all easy to define either the requirement or the ability to fulfil it. The requirements depend [5] upon the way in which the material is to be used and the conditions to which it will be exposed. Thus, they are very different, for example, for bricks (a) in an internal wall, (b) in an external wall with eaves protection and (c) in a parapet coping; bricks which might fail in one or two years under condition (c) might be quite satisfactory for 50 years in the protected external wall (b) and for ever in the internal wall (a). Calcium silicate bricks have only been made for about 60 years, but experience in practice and practical trials under severe conditions have shown the better qualities to be very durable even for use in positions of severe exposure. Since all bricks of this type have similar pore structure, the resistance to frost action is dependent mainly upon the effectiveness of bonding, i.e. upon the strength. Bricks with a compressive strength, tested in the wet condition, of more than 3000 lb/in² can be regarded as suitable for the more severe conditions of exposure, and those of more than 2000 lb/in² as suitable for normal external facing work.

The hydrous calcium silicates have, as shown elsewhere, a very small but real solubility in water and can be completely decomposed by dilute acids. Calcium silicate bonded bricks cannot normally, therefore, be regarded as suitable for use where exposed to flowing water, to one-sided water pressure, or to acids. This solubility effect is not sufficient to have

any significant
soil water.

The fire
lime brick
good cond
reduction:
ture above
expansion
cause colla
is much at
are, in fac
for, and as
silicate bo
shown in
most likel
have them

T
The fac
subject of
procedure
known. Th
paragrap
compressi
soaked in
on such c
on a com
condition

The str
aggregate
agent, at
a minimu
decreas
relat
in
another.

This fo
bonded m
in this in

any significant adverse effect in exposure to rainfall or in exposure to the soil water in foundation work.

The fire resistance of calcium silicate bricks is good; in practice, sand-lime brick walls of burned out buildings have often been in sufficiently good condition for incorporation in rebuilding. There is a considerable reduction in strength of those parts of the material reaching a temperature above 575°C , the α - β quartz inversion temperature, due to the expansion on inversion, but this drop in strength is not sufficient to cause collapse or disintegration. The softening temperature of the bricks is much above anything reached in a normal fire, and sand-lime bricks are, in fact, sometimes used for refractory purposes. They are suitable for, and are used for, chimneys, furnace casings, flues, etc. The calcium silicate bonding material itself is dehydrated at high temperatures, as shown in Volume 1, Chapter 5, but the dehydration products, which are most likely to be wollastonite ($\text{CaO} \cdot \text{SiO}_2$) or rankinite ($3\text{CaO} \cdot 2\text{SiO}_2$), have themselves a bonding value.

A. THE FACTORS AFFECTING QUALITY OF CALCIUM SILICATE BONDED BRICKS

The factors influencing the strength of sand-lime bricks have been the subject of numerous papers [3, 6-9] and are, so far as the established procedure of manufacture is concerned, for the most part now clearly known. The major factors and their effects are described in the following paragraphs. Unless otherwise indicated, the strength values quoted are compressive strengths on small cylinders prepared in the laboratory and soaked in water for 24 hr before testing in the wet condition. Strengths on such cylinders are usually a little below those of full size bricks made on a commercial plant from the same mix and under the same nominal conditions, also tested wet.

1. Lime Content

The strength obtainable with any product consisting of a strong aggregate and a strong binding agent increases with content of binding agent, at first rapidly, until all the surfaces of aggregate are bonded and a minimum of voids is achieved, then slowly, with possibly a slight decrease with very high proportions of binder, depending upon the relative inherent strengths of the two materials and of the bond one to another.

This form of relation holds for the lime content in calcium silicate bonded materials, and Fig. 1 shows a typical curve for a sand-lime mix, in this instance with a rather fine and uniform sand [10]. The values of

the maximum strength point, both in respect of actual strength and optimum lime content, depend mainly upon the characteristics of the sand. Thus, a coarser sand would have both lower optimum lime content and lower maximum strength, while a sand of similar median particle size but better grading would give a similar or higher optimum lime content and higher strengths. Within the normal range of lime content (4-12% CaO) the strength is generally so related to lime content that it can be taken for practical purposes as directly proportional.

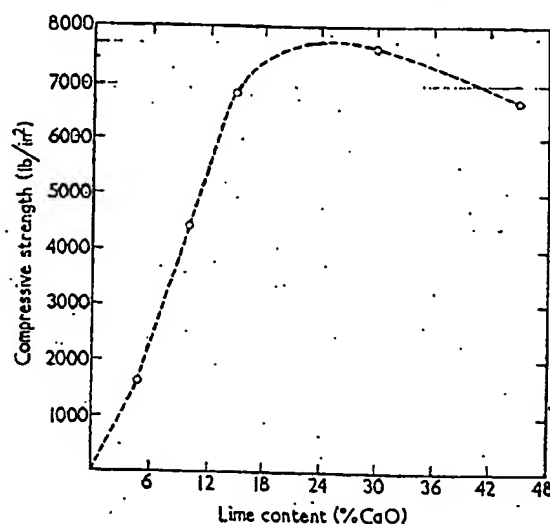


FIG. 1. An example, for a given fine sand, of the effect of lime content upon strength of sand-lime brick.

2. Lime Quality

It is generally desirable for the lime used to be a high-calcium lime of reasonable purity [11, 12]. Expansion of any hard-burnt MgO in limes of high MgO content is likely to give trouble on hydration in the autoclave. Generally, 3% MgO is taken as a limit, but Wuhrer, Steyer and Rodermacher [13] have recently shown that, if the lime is lightly burnt, considerably higher amounts can be tolerated. The other significant impurities in lime produced from natural materials (limestone or chalk) are silica, alumina and iron oxide, mainly present as their calcium compounds. These impurities are only of indirect importance in that they reduce the amount of calcium available to form the calcium silicate bond.

The alumina present as $\text{Ca}(\text{SiO}_3, 2\text{H}_2\text{O})$ has no bondi

Any unburnt lime is significant in efficiency of calcium oxide control test

The natural practice, the

FIG. 2.

particle size quantity and impurities, brick.

A wide range of grain

The alumina present as gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) is inert, but any present as calcium aluminate may form hydrogarnet ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot (\text{SiO}_2, 2\text{H}_2\text{O})_3$), which takes up a relatively high proportion of lime and has no bonding value.

Any unburnt limestone or chalk in the lime acts as a diluent or filler and is significant only as reducing the amount of useful or "available" lime. The latter is determined by a recognized empirical titration method, which in effect gives the amount of calcium which is present as free calcium oxide or hydroxide or which is readily formed by hydrolysis of calcium silicates etc. The available lime content thus serves as a useful control test of the value of a lime for this purpose.

3. Sand or Aggregate Quality

The nature and quality of the sand or other aggregate used is, in practice, the most important factor affecting quality. The grading of

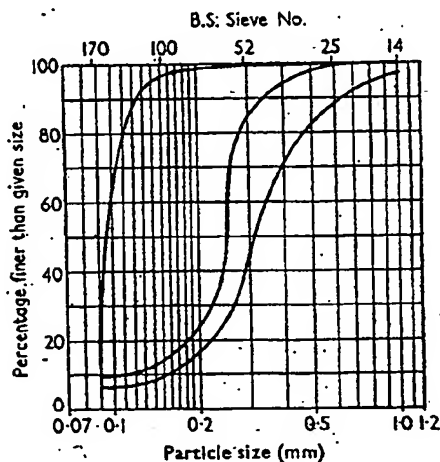


FIG. 2. The grading of typical natural sands used in calcium silicate bonded (sand-lime) bricks.

particle size, the particle shape, the surface characteristics and the quantity and nature of any mineral matter other than quartz, or of other impurities, may each have very great effects upon the properties of the brick.

A wide range of particle size is desirable for good results, the maximum size of grain and the amount of coarser material desirable depending

upon the texture required and upon limitations induced by problems of pressing the units; generally, a maximum size of about $\frac{1}{4}$ in (6 mm) can be tolerated. At the other end of the size scale, presence of an appreciable proportion of fine silica flour is advantageous; indeed, very high strengths can be achieved only when there is a fairly high content of very fine silica. The grading curve should be such as to give a low porosity when compacted; this may be achieved either with continuous grading or gap-grading. Most natural sands are closely graded and do not therefore satisfy these conditions. It is therefore often advantageous to blend

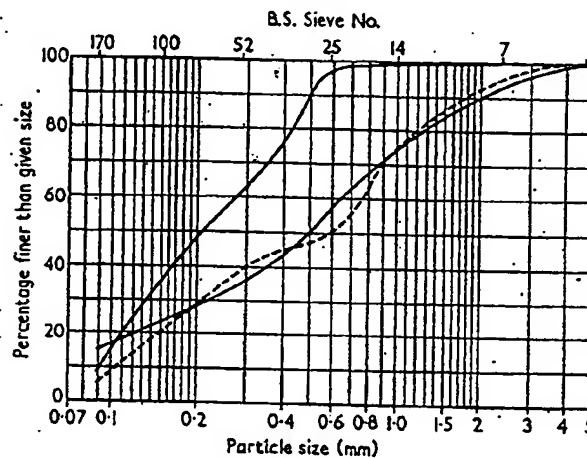


FIG. 3. The grading of samples of blended sands, or of crushed flint and sand, used to give high-strength calcium silicate bonded bricks.

two different sands or other fine aggregates of different average particle size or to grind a portion of the sand, if it is originally coarse enough, in order to broaden the range of sizes. Figure 2 shows the grading curves of some natural sands used in calcium silicate brick manufacture. Figure 3 shows some grading curves of blended sands or crushed flint and sand used to give higher strength bricks. Although detailed consideration of the procedures is outside the scope of this book, the grading, where the available raw materials permit, can now be designed to enable the producer to make bricks of any required strength within the normal range of needs.

The sand used also affects the drying shrinkage of the bricks, the three factors involved being the amount of clay impurity, the fineness and the surface characteristics of the sand grains.

The materials
the amount of w
in the hand. The
aggregate and w
It is not highly

Wet compressive strength (lb/in²)

FIG. 4

significantly ex
of the whole m
The mouldin
100 tons on ea
and the wear o
moulding pres
mixes, the deg

4. Pressing Conditions

The materials for calcium silicate bricks are mixed to a damp condition, the amount of water being such that the mix just coheres when squeezed in the hand. The water content varies somewhat with the fineness of the aggregate and with the lime content, but is generally between 4 and 7%. It is not highly critical up to an optimum value, but if this amount is

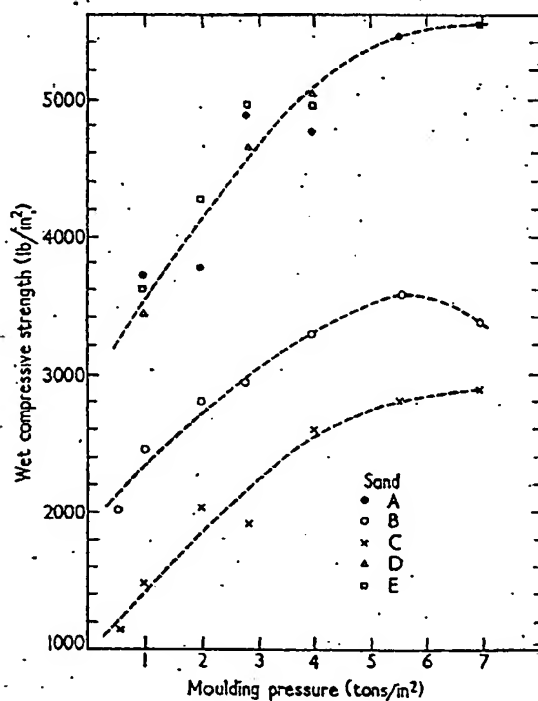
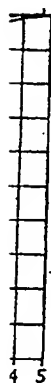


FIG. 4. The effect of moulding pressure upon the strength of sand-lime bricks.

significantly exceeded, bursting of the bricks and even complete collapse of the whole mass of bricks can occur in the autoclave.

The moulding pressure normally used is about 2–3 tons/in², i.e. about 100 tons on each brick. The machines have therefore to be very robust and the wear on the liners of the brick moulds is very severe. These high moulding pressures are necessary to achieve, with these non-plastic mixes, the degree of compaction necessary. Figure 4 shows the variation

by problems of
in (6 mm) can
an appreciable
high strengths
it of very fine
porosity when
us grading or
not therefore
ous to blend



flint and
ricks.

average par-
tially coarse
s the grading
anufacture.
crushed flint
etailed con-
the grading,
ed to enable
the normal

bricks, the
the fineness

of strength with moulding pressure for several sands. From these results it would appear to be worth while increasing pressures to about 4 tons/in². In practice, however, the additional cost of the machine and the increased maintenance costs make this a less economic method of achieving increased strength than other methods.

5. The Conditions of Steam Hardening (Autoclaving)

The conditions of steam hardening used in commercial practice are determined primarily by economic considerations. These include the

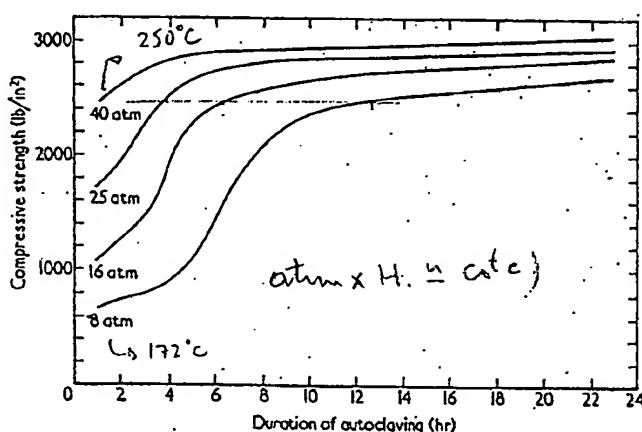


FIG. 5. The effect of duration of steam hardening (autoclaving) upon the strength of a calcium silicate bonded brick (6% CaO content) at various pressures, after Gunzelmann [8]. (absolute pressure!!)

amount of fuel required, the capital cost of the plant needed and its throughput, and the labour involved. The extremes of conditions used range from about 20 hr at full steam pressure, with the lowest pressures of about 8 atm (120 lb/in²), down to about 2 hr at pressure with the highest pressures of about 25 atm (350 lb/in²). The very high pressures have been used only in a very few recent plants in Germany, the normal range both in the U.K. and abroad being from 8 to 13.5 atm (120–200 lb/in²). It has been shown by several investigators [8, 14, 15] that over the practical range of steam pressures the same degree of hardening, as measured by the compressive strength of the product, can be obtained by varying the time appropriately. The curves in Figs. 5 and 6 illustrate this. It is also apparent from Fig. 5 that for each pressure there is a

steaming time beyond which it is not worth while to justify the additional cost of the plant. It is found that a plant of the designed work:

Going beyond the work of Pohl [15] has shown that at the higher pressures the hardening takes place at a high rate and the hardening is continuous.

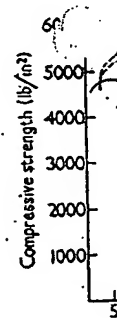


FIG. 6. The effect of duration of steam hardening (autoclaving) upon the strength of a calcium silicate bonded brick (6% CaO content) at various pressures, after Gunzelmann [8]. (absolute pressure!!)

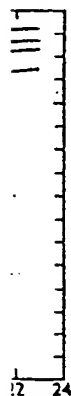
These conclusions, which have been confirmed by values obtained in practice, will be noted that the strength is much more sensitive to these lower pressures than to the higher ones. They are no doubt the result of a phase change or an inversion in the section of this change.

B. THE

Despite the very high compressive strength of calcium silicates, the microstructure of the bricks is early in the

these results
at 4 tons/in².
and the in-
d. of achiev-

g)
pr...ce are
i...de the



upon the
st...vious

ded and its
ditions used
est pressures
ure with the
gh pressures
; the normal
tm (120-200.
5] that over
ardening, as
be obtained
d 6 illustrate
re there is a

steaming time beyond which the gain in strength is no longer sufficient to justify the additional cost of further steaming. It is usual therefore to find that a plant operates on a fixed time of steaming, depending upon the designed working pressures of the boiler and of the autoclaves.

Going beyond the periods of autoclaving used in commercial practice, Pohl [15] has shown, in tests at 8, 16 and 21 atm autoclave pressure, that at the higher hardening pressures, although the increase in strength takes place at a higher rate, the maximum strength achieved is lower; if hardening is continued too long, a reduction in strength is liable to occur.

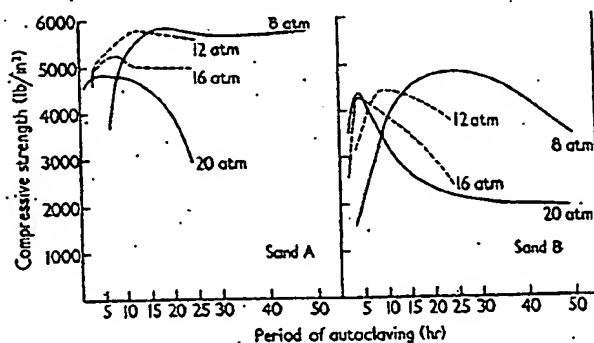


FIG. 6. The effects of time and pressure of autoclaving upon strength of sand-lime bricks (periods up to 48 hr).

These conclusions, which did not appear from Gunzelmann's work, have been confirmed by the present author, and the curves of Fig. 6 show the values obtained with two different sands, with 10% hydrated lime. It will be noted that the drop in strength with long periods of autoclaving is much more marked with one sand than with the other. The causes of these lower strengths at higher pressures have not yet been proven, but they are no doubt due to changes in the hydrated calcium silicate, which may be either a change in the crystal form or structure of the tobermorite or an inversion (for example, to xonotlite), as discussed in the next section of this chapter.

B. THE CONSTITUTION AND MICROSTRUCTURE OF CALCIUM SILICATE BRICKS

Despite the very large amount of fundamental work on the hydrated calcium silicates themselves, there has been relatively little on the microstructure and constitution of the actual bond in calcium silicate bricks. Early investigators [16, 17] in optical microscope studies observed

both crystalline and amorphous material, but it is not now clear how much of the crystalline material observed was calcite.

Smirnov [18] in 1926 reviewed earlier work and showed the presence of a hydrated silicate as fine "scales" of low birefringence with refractive indices between those of quartz ($n = 1.544$) and microcline feldspar ($n_m = 1.523$). He observed also that the silicate was readily converted to carbonate (calcite) on exposure, so that in old bricks much, if not all, of the lime content was present as carbonate. His analyses, for lime, soluble silica and carbonate content, show, after allowing for CaCO_3 , the molar ratios in the silicate given in Table III.

TABLE III

The range of composition of the bonding material in sandlime bricks

Author	Ratio of combined lime to soluble silica	Ratio of combined water to soluble silica
Smirnov [18]	0.99-1.27	1.65-1.99
Bessey [3]	0.97-1.77	—
Bessey [55]	0.83-1.86	0.88*-2.22*
Kalousek [22]	0.99-1.75	—

* Dried in *vacuo* at about 80° C.

Grime and Bessey [19] in 1933, from X-ray, chemical and optical examination, concluded that the bonding agent was an amorphous hydrated calcium silicate, but the equipment and the information available to them were inadequate to show the more diffuse patterns of tobermorites or to distinguish them in the presence of calcite and quartz. The Building Research Station published in 1939 [20] photomicrographs showing that in some commercial bricks the bonding material was amorphous, so far as resolution in the optical microscope could show, but that in others (rather uncommonly) there was a fine short needle-like growth of crystals. Plate 1 shows one of these photomicrographs of the crystalline material. Unfortunately, no X-ray diffraction results were obtained on this material.

Bessey [3] in 1948 indicated that the more crystalline silicate bond was found in bricks made with sand which, because of some undetermined grain surface condition, was less reactive than that which gave the more amorphous bond. The bricks containing the more crystalline material had lower drying shrinkage. He found in this work, done in 1938-9, that the lime/combined silica ratios in a range of 21 different commercial

TABLE IV

The amount and composition of the bonding material in some commercial calcium silicate bricks [55]

Determined values	Calculated values		Calculated compressive strength
	Molar ratio of combined	silica	

is not now clear how
te.
showed the presence
gence with refractive
microcline feldspar
readily converted to
as much, if not all, of
analyses, for lime,
for CaCO_3 , the

aterial in

ratio of
ned water
able silica

5-1.99

1*-2.22*

chemical and optical
was an amorphous
d the information
di e patterns of
ate and quartz.
[photomicrographs
ding material was
scope could show,
ne short needle-like
micrographs of the
action results were

ie silicate bond was
ome undetermined
high gave the more
rystalline material
one in 1938-9, that
ferent commercial

16. CALCIUM SILICATE PRODUCTS

115

TABLE IV
The amount and composition of the bonding material in some commercial calcium silicate bricks [55]

Sample No.	Determined values					Calculated values				Calculated compressive strength for each 1% soluble silica
	Total lime (as CaO) (%)	Combined silica (as SiO_2) (%)	Free lime (as CaO) (%)	Loss at 1000°C (%)	Carbon dioxide (%)	CaO as silicate (%)	Silicate cementing material (%)	Molar ratio of combined lime to water to combined silica		Compressive strength of bricks (lb./in. ²)
								combined silica	combined silica	
18	14.08	15.67	0.07	4.86	0.71	13.11	32.32	0.80:1	0.88:1	6768
17	12.98	12.98	0.06	4.93	0.63	12.12	29.38	1.00:1	1.10:1	5468
19	12.88	12.27	0.07	4.88	0.70	11.91	28.34	1.04:1	1.13:1	4355
63	9.78	8.78	Nil	4.33	0.67	9.06	21.60	1.12:1	1.43:1	2380
16	9.01	8.66	0.01	4.36	0.41	8.68	21.29	1.07:1	1.52:1	3135
131	8.70	7.90	Nil	3.87	0.10	8.67	20.24	1.16:1	1.69:1	8870
22	9.24	8.54	0.07	3.66	0.64	8.36	19.90	1.05:1	1.17:1	4030
61	8.02	7.15	Trace	3.76	0.42	7.49	17.98	1.13:1	1.54:1	3740
32	7.92	7.91	Trace	2.97	0.75	6.97	17.10	0.94:1	0.94:1	5210
26	7.59	6.10	0.01	3.53	0.49	6.96	16.10	1.22:1	1.66:1	5130
65	7.32	6.26	Trace	3.49	0.40	6.74	16.02	1.16:1	1.62:1	5560
29	7.39	6.05	0.04	3.19	0.55	6.65	15.33	1.18:1	1.45:1	5030
138	6.91	6.28	Nil	3.26	0.55	6.21	15.20	1.06:1	1.44:1	5550
132	6.76	7.26	Nil	3.07	0.64	4.95	14.63	0.83:1	1.26:1	5410
181	8.07	5.00	0.12	4.54	1.27	6.34	14.67	2.22:1	2.22:1	1480
21	6.93	6.58	Nil	2.49	0.51	6.28	13.84	0.86:1	1.00:1	4508
33	6.73	5.00	Trace	3.04	0.99	5.48	12.53	1.18:1	1.36:1	2620
34	6.99	4.03	0.01	3.76	1.47	5.12	11.43	1.36:1	1.69:1	1620
46	4.44	4.55	Nil	3.02	0.84	3.63	10.56	0.85:1	1.70:1	5480
28	7.60	3.72	1.25	3.83	1.40	4.57	10.30	1.31:1	1.80:1	1308

bricks varied over the range given in Table III. The more recent results by the present author, derived from Table IV, are also given in Table III.

Taylor [21] in 1952 reported X-ray evidence of the presence of a tobermorite-type compound in a commercial lightweight sand-lime block; the lime/soluble silica ratio in this material was 1.28. Kalousek [22], using X-ray diffraction, differential thermal analysis and soluble silica determinations on lime:sand specimens made up and autoclaved under a

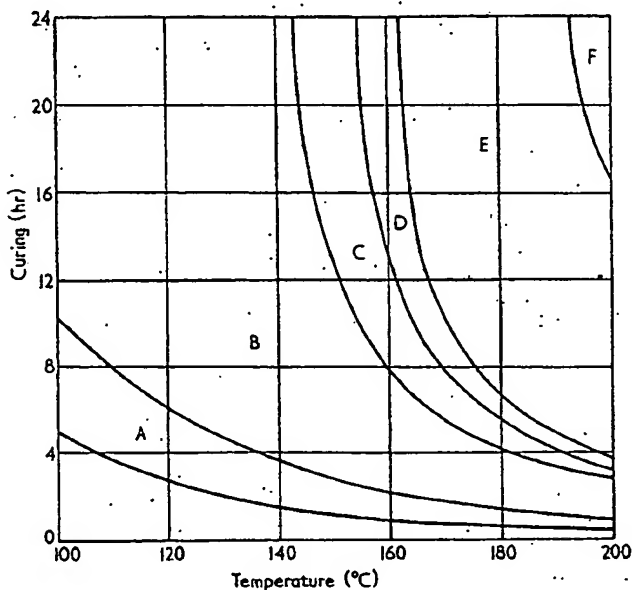


FIG. 7. The phases detected in autoclaved lime-quartz pastes (Neese [26]).
 A— $O_{1.75}SH_n + Ca(OH)_2 + \text{quartz}$; B— $C_{1.25}SH_n + Ca(OH)_2 + \text{quartz}$;
 C— $C_{1.25}SH_n + \text{quartz}$; D— $C_{1.0}SH_n + \text{quartz}$; E— $C_{1.0}SH_n + \text{tobermorite} + \text{quartz}$; F—tobermorite + quartz.

variety of conditions, found (Table III) lime/soluble silica ratios similar to those found by Bessey. When the ratio was below 1.3 only tobermorite was found, but when the ratio exceeded this figure the DTA results indicated gradual crystallization of α -dicalcium silicate hydrate. Further work [23, 24] showed that the reaction proceeded through a series of steps, starting with the formation of badly crystallized C-S-H (II) having a high lime/silica ratio, followed by C-S-H (I) with a lower lime/silica ratio and crystalline tobermorite. Neese and his co-workers [25, 26], using chemical, optical, X-ray, DTA, thermogravimetry and

dilatometry methods quartz, came to similar results reported for the times commonly used in the curves do vary with the lime/silica, but they show Aitkin and Taylor a CaO/SiO_2 range of from 90° to 200° C (1-compounds shown in

Compounds

Compound

Gyrolite
 C-S-H (ill-crystallized)
 Tobermorite
 (crystalline 11 Å)
 Xonotlite
 "Phase F"
 α -C₂S-hydrate
 Hillebrandite

Quincke [28] published the action of the lime fibres, probably of patterns which, he is of gyrolite.

The general picture as occurring in the ignoring for the moment in industrial raw materials as follows:

"Although many obscure, and other picture seems now grains yields initial similar in composition

re recent results
ven in Table III.
e presence of a
sand-lime block;
ousek [22], using
ble silica deter-
cl and under a

dilatometry methods on autoclaved pastes of lime and finely divided quartz, came to similar conclusions. Figure 7 shows an example of the results reported for the phases found over the range of temperatures and times commonly used in calcium silicate brick manufacture. The positions of the curves defining the various areas are not precise and must vary with the lime/silica ratio of the mix and the surface area of the silica, but they show clearly the progressive changes that occur.

Aitken and Taylor [27] examined products of lime-quartz pastes over a CaO/SiO_2 range of from 0.33:1 to 3.00:1 at autoclaving temperatures from 90° to 200°C (1–15 atm pressure) and observed the formation of the compounds shown in Table V.

TABLE V

Compounds detected in lime-quartz pastes (Aitken and Taylor [27])

Compound	Overall CaO/SiO_2 ratios of pastes in which detected	Range of temperatures in which compound was formed (°C)
Gyrolite	0.33–0.67	165–200
C-S-H (ill-crystallized)	0.33–3.00	90–175
Tobermorite (crystalline 11 Å form)	0.33–1.08	125–200
Xonotlite	0.67–3.00	165–200
"Phase F"	1.00–3.00	165–200
α -C ₂ S-hydrate	1.50–3.00	125–175
Hillebrandite	1.67–2.00	165–200

Quincke [28] published some excellent electron micrographs showing the action of the lime on the quartz surface and the formation of matted fibres, probably of tobermorite. He also gives electron diffraction patterns which, he suggests, show formation of 11.4 Å tobermorite and of gyrolite.

The general picture of existing knowledge on the lime-quartz reaction as occurring in the process of hardening of calcium silicate bonded bricks, ignoring for the moment the effects of the impurities which are inevitable in industrial raw materials, has been clearly summed up by Taylor [29] as follows:

"Although many details of the lime-quartz reaction in pastes are still obscure, and others depend on the precise working conditions, the general picture seems now to be fairly clear. Reaction on the surfaces of quartz grains yields initially a lime-rich poorly crystallized tobermorite mineral, similar in composition to C-S-H (II) made in suspensions. When the

Neese [26]).
)₂ + quartz;
tobermorite

ratios similar
3 only tober-
ure the DTA
icate hydrate.
led through a
allized C-S-H
with a lower
is co-workers
avimetry and

overall Ca/Si ratio is low, this reaction proceeds until all the lime is used up; the C-S-H (II) then reacts with more quartz giving C-S-H (I), the Ca/Si ratio of which eventually drops to 0.8. If the temperature and time of autoclaving are sufficient, the C-S-H (I) recrystallizes to tobermorite and eventually to xonotlite. Tobermorite has been detected in pastes cured at 125° C and above, and xonotlite at 165° C and above, but higher temperatures are needed in each case to make the reaction proceed at a technically useful rate. If the overall Ca/Si ratio is below 0.8, the C-S-H (I) or tobermorite also reacts slowly with the unused quartz to give gyrolite.

"When the overall Ca/Si ratio is above 1.0, C-S-H (II) is probably still the initial product. In this case, however, even before all the quartz is used up, the C-S-H (II) begins to recrystallize into other lime-rich phases. The most usual of these is α -C₂S hydrate. Crystallization of this phase is probably gradual, and there is evidence that its composition can depart from the ideal value, at least in the early stages of formation. Other lime-rich phases may also be formed but less reproducibly; further work is needed on this aspect of the problem."[†]

The second paragraph of this quotation refers to conditions that never truly hold for a commercial brick composition, but since the ratio of lime to available silica will depend upon the area of surface exposed and hence upon the fineness of the sand, it may well be that the effective ratio of Ca to Si during the period of reaction does exceed 1.0 even though the ratio of lime to total SiO₂ is probably less than 0.1.

The kinetics of the reaction of lime and quartz have so far been given little attention and very little information has been published. There is considerable variation in the rate of reaction, both with surface area of the silica and with reactivity of the surface of the sand grain. Table VI shows the amounts of silica reacted, after raising the autoclave to 10.7 atm (157 lb/in²) pressure in 1 hr and holding it at that pressure for only 15 min, with a mix of 10% hydrated lime and 90% various sands. Freshly crushed quartz crystal (samples 58, 59, 66 and 67) is more highly reactive than most of the natural sands; when, however, all particles below 100 mesh were removed, the amount of reaction in this period was small. There is evidence of a relation between the drying shrinkage of bricks made with these sands and the rate of formation of soluble silica, particularly with the pure quartz. With the most active sample of crushed quartz the amount of silica which had reacted (4.3%) in this short time was more than half of the amount which would react with long autoclaving.

The effects of the impurities in lime and natural sand upon the con-

[†] Nomenclature slightly altered to agree with that used elsewhere in this book.

stitution have not been adverse effects upon hydrogarnet (3CaO . A also suggested that si conditions, enter the t in the manufacture o ducers have to deal w the effects of small an minerals, hydrated al carbonates and sulph

Rates of reaction of
15

	Sand sample no.
Crushed quartz	59
	58
	66
	67 siev mes
Natural sand	51
	54
	50
	64
	65
	65

C. THE RELATIVE MATERIAL AND TIME

While the evidence silica ratios vary only sand-lime bricks, the overall chemical comp phases, the crystal for cell dimensions, may properties are materia

stitution have not been widely studied. Clay minerals are known to have adverse effects upon the properties of the bricks, probably because of hydrogarnet ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot (\text{SiO}_2, 2\text{H}_2\text{O})_3$) formation. Kalousek [30] has also suggested that small amounts of alumina may, under appropriate conditions, enter the tobermorite lattice and modify its properties. Since, in the manufacture of calcium silicate bonded products generally, producers have to deal with impure natural products, further research into the effects of small amounts of the common natural impurities, i.e. clay minerals, hydrated alumina, hydrated iron oxide, magnesia, and alkali carbonates and sulphates, could be fruitful.

TABLE VI

Rates of reaction of sands with lime (proportion of silica reacted after 15 min at 157 lb/in² steam pressure)

	Sand sample no.	Reacted silica (SiO ₂ , %)	Drying shrinkage of bricks made with same sand with 6 hr autoclaving (%)
Crushed quartz	59	1.3	0.028
	58	2.8	0.045
	67	4.3	0.054
	67 sieved on 100 mesh B.S. sieve	0.4	n.d.
Natural sand	51	0.5	0.018
	54	1.4	0.015
	50	0.9	0.031
	64	2.3	0.028
	65	1.3	0.005
	55	3.4	0.033

C. THE RELATION BETWEEN COMPOSITION OF THE BONDING MATERIAL AND THE TECHNICAL PROPERTIES OF THE PRODUCT

While the evidence suggests that the lime/silica and combined water/silica ratios vary only over a narrow range in the bonding material in sand-lime bricks, the phase composition may vary much more than the overall chemical composition. Even within the range of tobermorite-like phases, the crystal form, the crystal size, and even the composition and cell dimensions, may all vary to such an extent that the technical properties are materially affected. In some products, xonotlite, gyrolite,

all the lime is used in C-S-H (I), the temperature and time varies to tobermorite detected in pastes above, but higher reaction proceed at a low 0.8, the C-S-H and quartz to give

is probably more all the quartz than other lime-rich composition of this composition can give of formation as reproducibly;

conditions that it since the ratio surface exposed that the effective exceed 1.0 even than 0.1.

so far been given blished. There is a surface area of grain. Table VI indicates to 10.7 are for only various sands.

is more highly er, all particles this period was ng shrinkage of of soluble silica, tive sample of (4.3%) in this react with long

upon the con- a this book.

α -C₂S hydrate and perhaps other phases may replace the tobermorite-like phases and have major effects upon properties. Also, in these commercial materials the introduction into the gel or crystal structure of aluminium or other ions by isomorphous substitution may change the properties. Although much remains to be learnt of these effects, something is known of them, in particular from the work of Kalousek [23, 30] and that of Sanders and Smothers [31], as indicated below.

1. Strength

The strength of bond given by the various hydrated calcium silicates varies very widely. This variation is discussed generally in Volume 1, Chapter 11, and only the information available on those compounds which may be important in products made directly from lime and silica need be considered here.

The evidence from the observations of Menzel [32], Sanders and Smothers [31] and Kalousek and Adams [33] on the strength of Portland cement and fine silica mixes have demonstrated the relatively low strength of α -C₂S hydrate.

Kalousek and Prebus [24] showed that crystallized tobermorite gives higher strength than C-S-H (I). There is also evidence from the present author's work that a lower lime/silica ratio in the C-S-H corresponds to higher strengths, but it is difficult to separate this effect from that of the crystallization of the tobermorite.

Kalousek [34] has found satisfactory strengths with a xonotlite bond, but no direct comparisons with tobermorite are available.

2. Drying Shrinkage

The most important difference in drying shrinkage is that between C-S-H (I) and crystalline tobermorite [24]. This accounts for the substantial difference between concretes cured at ambient temperatures or in low-pressure steam and those cured in the autoclave, and for the relatively low drying shrinkage of calcium silicate bricks. α -Dicalcium silicate hydrate and xonotlite are both known to have still lower drying shrinkage than tobermorites, but there is still a wide area of uncertainty needing further study of the effect upon this property of variations within the tobermorite range of composition and with varying degree of crystal growth.

3. Other Properties

No other important technical properties of calcium silicate bricks are known to be significantly affected by the nature of the silicate bond.

III. A.

The achievement in structural build attempts by purpose before hardening, known as aerated,

Various methods fall into one of two chemical action as of a stable foam or air-entraining.

Of the chemical aluminium powder lime may be present of Portland cement secondary product significant in the aluminate hexahydrate

2Al + 3

An alternative generation of oxygen and bleaching powder thus:

The foam injected to those used in which the bubbles are closely controlled mix, any required control. The method made on the building

The method in entraining agents achieve such low used for concrete

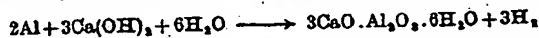
The earliest of material Aerocreminium powder. and, although of drying shrinkage

III. Aerated (Foamed) Calcium Silicate Products

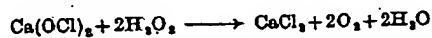
The achievement of light weight with adequate strength and durability in structural building materials has important advantages. Commercial attempts by purposeful incorporation of gas into cement bound products before hardening, to form the class of materials which have been variously known as aerated, foamed or cellular concretes, date from about 1925.

Various methods have been used for effecting aeration, but they all fall into one of two types: (a) the generation of a gas within the mix by chemical action and (b) the incorporation of air in the mix by injection of a stable foam or by whipping in air by suitable mixing devices using air-entraining agents in the mix.

Of the chemical methods of gas generation, the reaction between fine aluminium powder and lime, to generate hydrogen gas, is most used. The lime may be present as such in the mix or may be formed in the hydration of Portland cement used as binder. Calcium aluminates are formed as secondary products, but the amounts involved are not sufficient to be significant in the setting process. Assuming formation of tricalcium aluminate hexahydrate, the following equation expresses the reaction:



An alternative method, which has been utilized commercially, involves generation of oxygen gas by the reaction between hydrogen peroxide and bleaching powder, a mixture of $\text{Ca}(\text{OCl})_2$ and $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$, thus:



The foam injection process utilizes chemically stabilized foams similar to those used in fire fighting. By use of suitable foam generators, with which the bubble size and the amount of air to a given volume of liquid are closely controlled, and injection of a known volume of foam into a mix, any required density of product can be achieved, with good quality control. The method is, however, utilized more for aerated concretes made on the building site than for the factory-made autoclaved products.

The method in which air is whipped directly into a mix containing air-entraining agents cannot incorporate as much gas and cannot therefore achieve such low densities as the other methods mentioned. It has been used for concrete of a density down to about 80 lb/ft³.

The earliest of the aerated concretes, e.g. in the United Kingdom the material Aerocrete, were made with Portland cement, sand and aluminium powder. They were allowed to harden at ordinary temperatures and, although of reasonable strength, suffered from excessively high drying shrinkage. Later types (e.g. the Swedish products Siporex and

Ytong and the Danish Durox) were autoclave cured, the drying shrinkage being very much reduced thereby. With autoclaving it became possible to use lime instead of, or in part replacement of, Portland cement, the end-products of either bonding material being essentially the same. The choice of one or other depends largely upon economic factors and upon convenience in the process. Also, materials other than sand can be used, provided that they are sufficiently siliceous for reaction with the lime and sufficiently strong and stable in themselves. Thus, ground burnt shale (Ytong, Sweden) and pulverized fuel ash (Thermalite-Ytong and Celcon, United Kingdom) are both satisfactorily used. In order to produce material of the densities normally required, it is necessary for the aggregate to be very fine, with the greater part finer than 100 mesh (152 μ). If natural sand is used as aggregate, it is generally necessary to grind it to the required fineness.

The greater part of autoclaved aerated concrete production has in the past been in the form of building block, which, because of the lightness in weight, can be very much larger in size than the building brick, thus effecting economies in handling and in construction. The common size in most countries is equivalent to 12 bricks. More recently, however, use of large reinforced panels for wall and roof construction and in beams, lintels, etc. has become widespread. Development in this direction was at first slowed down by the need to overcome problems of corrosion of the reinforcement, which are naturally more serious than with dense concretes, but satisfactory durability is now generally accepted.

A. PROPERTIES

The aerated concretes have most often to compete commercially with lightweight concretes made by use of lightweight aggregates (clinker, foamed slag, expanded clay, sintered pulverized fuel ash, perlite, exfoliated vermiculite, etc.). A comprehensive study of both aerated and lightweight aggregate concretes including their properties and uses has been made by Short and Kinniburgh [35].

The normal range of technical properties of the aerated concretes is shown in Table II. In general, all properties are related to the density, which may be anything from about 25 lb/ft³ (400 kg/m³) upwards. In practice, grades of 30-35 lb/ft³ and of 45-50 lb/ft³ (480-560 kg/m³ and 720-800 kg/m³, respectively) are most commonly made; the former for use where thermal insulation is most important, and the latter where rather greater strength is required.

The strengths attainable are more dependent upon density than any other single factor, and, as indicated above, the densities at which these

materials are made are the strength required. strength requirement (28 kg/cm²). Table VII shows autoclaved aerated concrete may be seen that for the density of at least 35 strengths, can be used bearing.

The relation between

Dry density (lb/ft ³)	Cu
	(t
20	
30	
40	
50	

The low thermal conductivity of aerated concretes, giving them an alternative material for insulation, is independent of density. It is very slightly greater for those which have themselves (shale). Some typical values

The drying shrinkage of aerated concrete is to be higher than most and manufacturers have involved in keeping the found empirically to (a) the proportion of silica; (b) the particle size; (c) the autoclave curing conditions; by trial according to for drying shrinkage

cured, the drying
With autoclaving it
cement of, Portland
ial being essentially
gely upon economic
materials other than
siliceous for reaction
themselves. Thus,
uel ash (Thermalite-
isfactorily used. In
re ed, it is neces-
at part finer than
gate, it is generally

roduction has in the
ause of the lightness
building brick, thus
a. The common size
cently, however, use
ction and in beams,
n this direction was
lems of corrosion of
us than with dense
lly accepted.

a commercially with
aggr gates (clinker,
uel, h. perlite, ex-
of h aerated and
perties and uses has

aerated concretes is
ated to the density,
kg/m³) upwards. In
(480-560 kg/m³ and
ade, the former for
nd the latter where

on density than any
sities at which these

materials are made are usually fixed as low as possible consistent with the strength required. For load bearing building blocks the minimum strength requirement in the U.K. is generally taken as 400 lb/in² (28 kg/cm²). Table VII shows the manner in which the strength of typical autoclaved aerated concretes varies with density; from these figures it may be seen that for the above minimum strength of 400 lb/in² a concrete density of at least 35 lb/ft³ is necessary. Lower densities, with lower strengths, can be used for purposes in which the material is not load bearing.

TABLE VII

*The relation between density and other properties of aerated concrete
(Short and Kinniburgh [35])*

Dry density (lb/ft ³)	Cube crushing strength (tested wet) (lb/in ²)	Modulus of elasticity (lb/in ² × 10 ⁶)	Thermal conductivity (k) (B.t.u. ft ⁻¹ hr ⁻¹ in ⁻¹ deg F ⁻¹)
20	—	—	0.58
30	300	0.21	0.75
40	500	0.33	1.00
50	700	0.45	1.40

The low thermal conductivity is an important property of aerated concretes, giving them an advantage for many uses over most of the alternative materials. It is almost entirely a function of density and is independent of the nature of the bonding material (cement or lime), but it is very slightly greater with sand as aggregate than with aggregates which have themselves lower inherent conductivity (p.f. ash and burnt shale). Some typical values for various densities are shown in Table VII.

The drying shrinkage of the autoclave-cured aerated concretes tends to be higher than most other material used in brick or block construction, and manufacturers have to give considerable attention to the factors involved to keep the shrinkage as low as possible. Some of the factors found empirically to affect shrinkage for material of given density are: (a) the proportion of bonding agent, which should be as low as is practicable; (b) the particle size distribution of the aggregate; (c) the autoclave curing conditions (duration and pressure) which must be adjusted by trial according to the raw materials involved to give the best values for drying shrinkage consistent with economical production.

B. STRUCTURE AND CONSTITUTION

1. Structure

The macrostructure of a good aerated concrete (Plate 2) is in fact that of a solid foam with fine and nearly uniform round bubbles of air, held in a matrix of the very fine aggregate bonded together with the cementing medium. The air bubbles are in most processes originally hydrogen bubbles, but the hydrogen is rapidly lost by diffusion. The bubbles are not interconnected, except by very fine capillaries in the matrix, and water will not penetrate to them rapidly; dry aerated concrete will float for long periods in water before sufficient water penetrates to allow it to sink. This difficulty of saturation with water and the peculiar distribution of pore sizes together account for the remarkably high resistance to frost action of aerated concretes compared with other materials of similar strength. Even distribution of bubbles and uniformity of size are objectives which the manufacturer seeks to achieve, since the formation of some larger bubbles or the presence of irregular layers leads to lack of uniformity of quality of the product and to unsatisfactory mechanical and physical properties. It is also sought to ensure sphericity of bubbles since elliptical bubbles tend to cause variation of strength in different directions. The measures taken to control and ensure this uniformity and isotropy of structure are part of the closely guarded know-how of firms which have developed these materials.

The microstructure of the matrix of material, in which the air voids are embedded, is essentially the same when lime is used as the binder as in the dense calcium silicate bonded bricks, except that the aggregate is much finer. There are no published observations of crystalline structure visible in the optical microscope, and, because of the much higher surface area of the aggregate and the correspondingly higher rate of reaction of the lime and silica, it may be that the conditions for such visibly crystalline growth do not occur.

2. Phase Composition

Very little has been published on the phase composition of the bonding material in the aerated concretes, whether made with lime or Portland cement as binder. The examination by Taylor [21] of an aerated sand-lime block, in which he found a crystalline tobermorite and a $\text{CaO} \cdot \text{SiO}_2$ ratio of 1.28, has already been mentioned. In general, however, essentially the same course of phase formation may be expected as for the dense calcium silicate bonded bricks when lime is used with ground quartz sand as aggregate, and essentially the same as with autoclaved dense Portland cement concrete products when this cement is used.

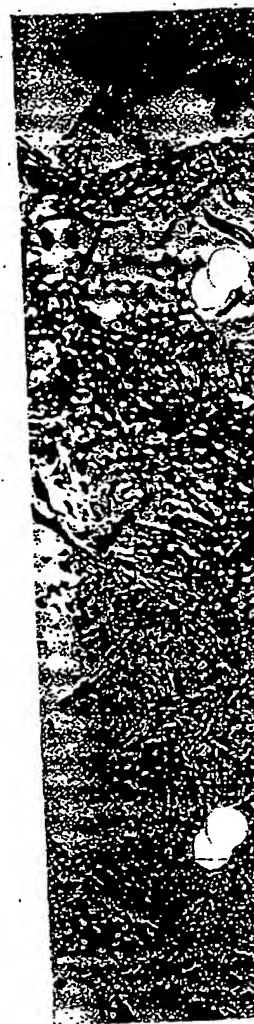


PLATE 1. Photomicrograph of needle crystals

2) is in fact that
 les of air, held in
 h the cementing
 inally hydrogen
 Th bubbles are
 the matrix, and
 oncrete will float
 tes to allow it to
 liar distribution
 sistence to frost
 erials of similar
 ity of size are
 e the formation
 leads to lack of
 ory mechanical
 icity of bubbles
 gth in different
 uniformity and
 ow-how of firms

h the air voids
 is the binder as
 he aggregate is
 ally structure
 h surface
 e of reaction of
 visibly crystal-

of the bonding
 re or Portland
 aerated sand-
 id $\text{CaO} \cdot \text{SiO}_2$
 ver, essentially
 for the dense
 round quartz
 occluded dense
 sed.



PLATE 1. Photomicrograph of calcium silicate bonded brick, showing
 needle crystals of hydrated calcium silicate ($\times 1620$, ordinary light).

IV. Calcium

Direct synthesis of hyc used in the manufacture asbestos as the aggregate hard, and strong sheet particularly in ships (wh extremely lightweight m thermal insulation of pi manufacture of these m published regarding than

Properties of cal

Type

A. Lightweight calcium silicate insulation

B. Calcium silicate bonded insulation board

(1) Fro

Diatomaceous earth, a asbestos and other ingre some types use is made o place between lime and c ing 100° C, to caus h ingredients when poure sufficient to allow the n After a period of curin pressures similar to thos other types the initial t being used, while the der considerable pressure to

Some properties of or insulation material and board are given in Table fire and are unaffected t

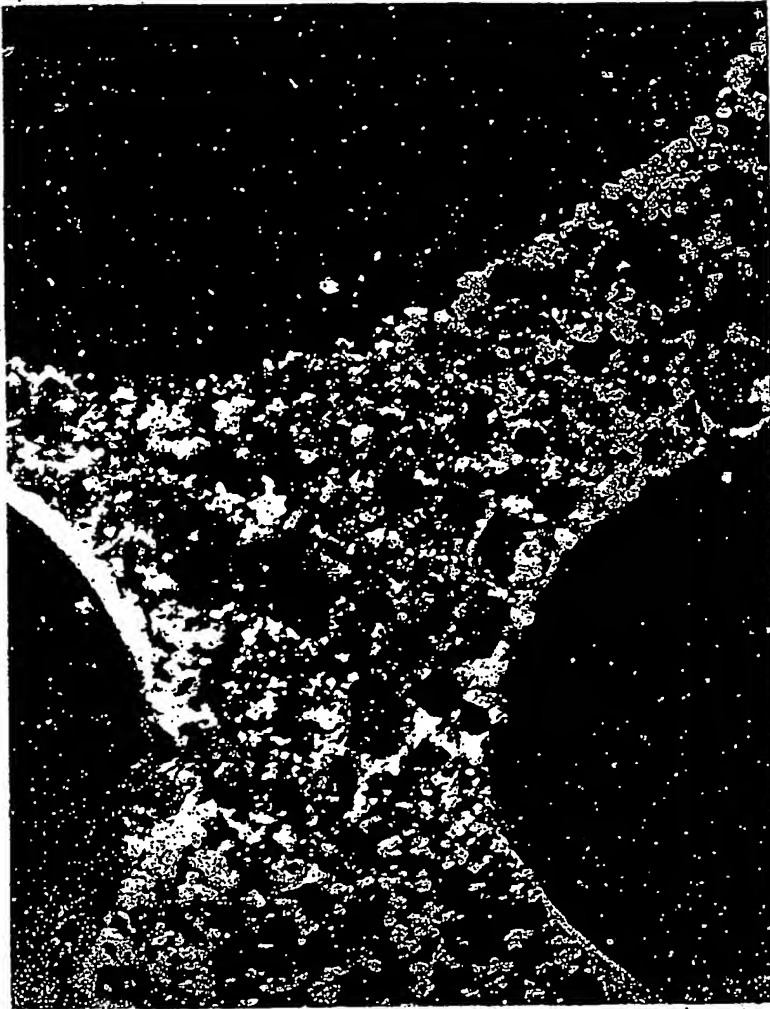


PLATE 2. Photomicrograph of aerated concrete, showing solid foam structure. ($\times 410$, crossed nicols)

IV. Calcium Silicate Bonded Asbestos Products

Direct synthesis of hydrated calcium silicate from lime and silica is used in the manufacture of a variety of proprietary materials with asbestos as the aggregate or as reinforcement. These range from dense, hard, and strong sheet materials used for wall and ceiling linings, particularly in ships (where their high fire resistance is valuable), to extremely lightweight materials in slab or moulded form, used for the thermal insulation of pipes, boilers, etc. The processes used for the manufacture of these materials are proprietary, and little has been published regarding them, except in trade literature.

TABLE VIII
Properties of calcium silicate bonded asbestos products¹

Type	Density (lb/ft ³)	Thermal conductivity at given temperature (B.t.u. ft ⁻² hr ⁻¹ in ⁻¹ deg F ⁻¹)		Maximum temperature of use	
		(°F)		(°F)	(C°)
A. Lightweight calcium silicate insulation	11½	200	0.36	1200	650
		400	0.48		
		600	0.58		
		800	0.65		
B. Calcium silicate bonded insulation board	44-48	Ambient	0.75	1000	540

(1) From data quoted by manufacturers.

Diatomaceous earth, a highly reactive form of silica, is used with lime, asbestos and other ingredients in making most of these materials. In some types use is made of the fact that a sufficiently rapid reaction takes place between lime and diatomaceous earth, at temperatures approaching 100° C, to cause within a few minutes a gelling of a mixture of these ingredients when poured into steam-heated moulds. The stiffening is sufficient to allow the moulded products to be removed and handled. After a period of curing in warm chambers they are autoclaved at pressures similar to those used in calcium silicate brick manufacture. In other types the initial heating in the moulds is omitted, stiffer mixes being used, while the dense boards are formed on machines which impart considerable pressure to compact the material.

Some properties of one type of the very lightweight calcium silicate insulation material and one type of calcium silicate bonded insulation board are given in Table VIII. These materials are resistant to heat and fire and are unaffected by steam, moulds or fungal growth, and organic



ag solid foam

solvents. The dense board types are also fairly resistant to acids and are less brittle than the types of asbestos board bound with Portland cement.

No work is known to have been published on the constitution of the bond in these materials. It seems likely that it is essentially the same as in other autoclaved calcium silicate products, but there may be some reaction with the asbestos minerals affecting the phase formation.

V. Very High Strength Calcium Silicate Bonded Products

Although, as shown in Table I, the currently manufactured range of calcium silicate bricks extends only up to about 8000 lb/in² compressive strength when tested in the wet state, equivalent to about 10,000 lb/in² if tested dry, this does not by any means indicate a practical limit of strength. In the author's laboratory wet strengths of up to 12,000 lb/in² have been shown to be practicable with economic mixes and conditions of processing. The Russian material Silicalcit, which is produced widely in the form of building slabs, beams, pipes, tiles and paving slabs; is claimed [36, 37] to have strengths of up to 20,000 lb/in²; the material developed in W. Germany, known as Poreen, in which pipes of large diameter and paving slabs have been made, is said [38] to have strengths of the order of 12,000 lb/in². Details of all these processes are at present undisclosed, but they are all, it is understood, essentially the same as the calcium silicate bonded bricks, apart from the fact that the materials and mixes are specially chosen or treated to attain the high strengths.

Further confirmation of the high strengths obtainable with hydrated calcium silicate has been obtained by Taylor [39]. Dry compressive strengths of pressed materials made in the laboratory, with very fine silica and lime, of as much as 20,000 lb/in² at a density of 100 lb/ft³ and 36,000 lb/in² at a density of 130 lb/ft³ have been found. The mixes were made at the optimum lime/silica ratio, given as about 0.14 + 0.00009 times the specific surface of the silica (cm²/g).

There appears to be considerable potential for development of use of autoclave-hardened calcium silicate bonded products based on lime as the raw material, into fields at present satisfied only by Portland cement products; in the U.S.S.R. such developments have already become important.†

VI. Calcium Silicate Fillers

Fillers are generally very fine inert powders included in compositions to modify the properties and to reduce consumption of more expensive active ingredients. The most important properties for this use are very

† See also Addendum (p. 133).

fine particle size and properties are not new sorts of filler. Although packing characteristic properties of the product.

Precipitated hydroxide in the rubber industry, since about 1 chemical composition in the control of quality. Other materials used

Effect of calcium silicate in rubber mix [41]. (Composition, calcium silicate)

Loading of calcium silicate (parts by weight)	Cur at 21 (m)
21	2
42	1
63	1
84	1

(1) Period

hydrous aluminium. Each has its particular

In rubber manufacture carbon black, which is rubber itself, in proportions of each the properties required for the product the abrasion another the tear strength under load and the by the filler. Although one type of filler, suitable properties in shape or

to acids and are
l with Portland

nstitution of the
ially the same as
re may be some
formation.

1. Products

actured range of
/in² compressive
out 10,000 lb/in²
practical limit of
p to 12,000 lb/in²
as and conditions
produced widely
paving slabs, is
in²; the material
ch pipes of large
to have strengths
ses are at present
y the same as the
the materials and
strengths.
le with hydrated
Dry compressive
y, with very fine
q 10 lb/ft³ and
l. The mixes were
out 0.14 + 0.00009

lopment of use of
based on lime as
Portland cement
already become

d in compositions
of more expensive
this use are very

fine particle size and high surface area; because of shape factors, these properties are not necessarily closely related when considering different sorts of filler. Although the fillers are inert, their surface energy and packing characteristics are extremely important in their effects upon the properties of the product.

Precipitated hydrous calcium silicates have been used as fillers, first in the rubber industry and subsequently in the paint and plastics industry, since about 1930. Fineness and surface properties, rather than chemical composition or constitution, have been given most attention in the control of quality during manufacture.

Other materials used as fillers include fine clays, precipitated silica,

TABLE IX

Effect of calcium silicate filler loading upon the properties of a natural rubber mix [41]. (Composition of mix: 100 parts natural rubber, 5 parts zinc oxide, calcium silicate filler as shown, 2 parts accelerators, 3 parts sulphur, 3 parts stearic acid)

Loading of calcium silicate (parts by weight)	Curing ⁽¹⁾ at 287° F (min)	Modulus at 300%	Tensile strength	Elongation at failure	Hardness	Tear strength (lb/in ²)
21	20	430	4000	700	45	300
42	15	710	3930	660	51	520
63	20	1120	3090	550	62	450
84	10	1220	2860	550	63	470

(1) Period of optimum curing as judged by tensile strength.

hydrous aluminium silicate, whiting and precipitated calcium carbonate. Each has its particular characteristics and advantages for specific uses.

In rubber manufacture any of these fillers is used with or in place of carbon black, which is normally the principal ingredient other than the rubber itself, conferring toughness and other useful properties. The proportions of carbon black and/or any particular filler used depend upon the properties required in the specific product being made. Thus, for one product the abrasion resistance may be of dominant importance, for another the tear strength, and for another the amount of elongation under load and the tensile strength. All of these properties are modified by the filler. Although, as mentioned above, the particle size is, for any one type of filler, the major variable affecting its value in conferring suitable properties to the product, for a given mean particle size, differences in shape or in chemical composition and structure may also be

important. For example, for shoe soles and heels it has been suggested [40] that certain resin-rubbers containing calcium silicate fillers wear better than those containing clay fillers.

As an example of the effect of the quantity of a calcium silicate filler upon the properties of a natural rubber mix, the data [41] reproduced in Table IX are of interest. The figures quoted should be regarded only as relative to each other, since they depend upon the qualities of the particular ingredients and upon the methods of test, but they serve to indicate the quantities of filler that may be usable.

A. MANUFACTURE

Since all calcium silicate fillers are made either by undisclosed proprietary processes or by patented processes, little can be said of them here. They are mostly, it is understood, based upon precipitation from sodium silicate solutions by calcium chloride, under closely controlled conditions of temperature, solution concentration and agitation. The sodium/silica ratio in the sodium silicate must be adjusted correctly. Washing of the precipitate after filtration, to remove sodium salts, must be very thorough and the drying method must be designed to avoid risk of overheating.

B. CHEMICAL COMPOSITION AND CONSTITUTION

The composition of some of the commercial silicate fillers is given in Table X. It is apparent from the lime/silica ratio that they are all essentially mixtures of hydrated silicates and hydrous silica; it is not known by the author whether this is because of expediency in manufacture or because their properties as fillers are better than those of a calcium silicate

TABLE X

Composition of some commercial hydrated calcium silicate fillers [44]

Trade name	CaO	SiO ₂	Analysis (per cent by weight)				pH
			CaO:SiO ₂ molar ratio	Na ₂ O	Loss at 105°C	Loss on ignition	
Anchor calcium silicate	16	60	0.29:1	—	3	17.5	10
Calsil	10-11	69-70	0.16:1	2.3	—	16	10
Silene EF	18	64	0.30:1	—	5	15	10
Silmos A ⁽¹⁾	18.1	45.2	0.43:1	—	8	19	9.8
Tufkmit	16.0	59.5	0.29:1	—	—	20	10.1

⁽¹⁾ Also contains MgO, Al₂O₃ and Fe₂O₃.

only. It is perhaps about 10, corresponding to SiO₂.aq., whereas (about 10.5 and 12, d pH values may be Table X are those of suspensions of about

The combined water range from 0.7 to 1. tobermorite and hydrous silica. Some of the fillers contain this is probably due to their content. On the other hand, in other of the fillers, where the precipitation of excess silica of low lime/silica ratio some time allowed tobermorite, but it is conditions operating at temperatures in the range [43], but no comment.

The user of filler is mainly with the surface area of the material as a surface area, considerable difference in the millimicron range present either as grains of hydrous silica or as the behaviour of fillers in the presence of silica.

C. PARTICLE SIZE

One of the chief considerations in the selection of fillers for rubber is the ductibility of particles and from a few figures quoted it may be seen that

as been suggested
licate fillers wear

cium silicate filler
[41] reproduced in
regarded only as
qualities of the
but they serve to

undisclosed pro-
be said of them
recipitation from
closely controlled
agitation. The
adjusted correctly.
odium salts, must
ned to avoid risk

UTION

fillers is given in
they are all essen-
; it is not known
a manufacture or
a cium silicate

icate fillers [44].

ght)	Loss on	pH
s at °C	ignition	
17.5	10	
15	10	
15	10	
19	9.8	
20	10.1	

only. It is perhaps significant that they all have an equilibrium pH of about 10, corresponding to the equilibrium between C-S-H (I) and $\text{SiO}_2 \cdot \text{aq.}$, whereas C-S-H (I) by itself would give pH values between about 10.5 and 12, depending upon the CaO/SiO_2 ratio [42]. These higher pH values may be unsuitable for some uses. The pH values shown in Table X are those quoted by the manufacturers and generally relate to suspensions of about 5% concentration.

The combined water/silica ratios, from the loss on ignition figures, range from 0.7 to 1.4. This is consistent with a mixture of C-S-H (I) or tobermorite and hydrous silica, dried at temperatures near to 100°C . Some of the fillers contain significant amounts of alkali (Na_2O) present—this is probably due to inadequate washing rather than to any intentional content. On the other hand, the presence of some MgO , Al_2O_3 and Fe_2O_3 in other of these products may be intended as modifying the properties.

Where the precipitation is made at fairly low temperatures in the presence of excess silica, the silicate phase will, it seems, be a C-S-H (I) of low lime/silica ratio (less than 1). If higher temperatures are used, with some time allowed for aging, there may be some crystallization of tobermorite, but it seems unlikely that this will be significant under conditions operating in industrial production. Treatment at higher temperatures in the autoclave will give tobermorite or even xonotlite [43], but no commercial fillers made in this way are known.

The user of fillers in the rubber and plastics industries is concerned mainly with the surface properties of the particles rather than with those of the material as a whole. Therefore, apart from the particle size and surface area, considered in a subsequent paragraph, there may be important differences in distribution of the calcium atoms which may affect the surface properties. Thus, it seems possible, even with particles in the millimicron size range, to have the calcium silicate (C-S-H (I)) present either as separate particles or as coatings on the surfaces of grains of hydrous silica. There has been a good deal of study of the behaviour of fillers in rubber [44, 45, 46] and some theoretical consideration of the nature of the surface and of the surface bond with hydrous silica.

C. PARTICLE SIZE, SURFACE AREA AND STATE OF AGGREGATION

One of the chief merits of the precipitated calcium silicates for use as fillers for rubber and plastics lies in the extreme fineness and reproducibility of particle size characteristics, which derive from the low solubility and from the control possible in the conditions of precipitation. A few figures quoted commercially are shown in Table XI, from which it may be seen that the particle size is generally in the range 20–50 μm .

with corresponding surface areas of some 50–150 m²/g. This is comparable with values for most of the carbon black fillers used in the rubber manufacturing industry.

Since the commercial fillers are, as already indicated, made up of two components, C-S-H (I) and hydrous silica, the shapes of the particles must be expected to be of two types, the two-dimensional sheet crystallites of C-S-H (I) (see Chapter 21 and Volume 1, Chapter 5) and granular or irregular particles of hydrous silica. There may therefore be a wide range of particle dimensions above and below the mean particle diameters quoted.

TABLE XI
Physical properties of some commercial hydrated calcium silicate fillers [44]

Trade name	Surface area (m ² /g)	Mean particle diameter (mμ)	Loose bulk density (lb/ft ³)	Specific gravity	Refractive index
Anchor calcium silicate	—	50	—	—	—
Calsil	—	40	9.4	2.05	—
Fortasil A70	105	30	—	2.1	—
Microcal 180	—	30–50	9	2.1	1.47
Microcal 210	—	30–50	12	2.0	1.45
Silene EF	80	30	12	2.1	1.47
Silmos A	140–160	—	—	2.0	—
Tufmit CS	50	—	11	2.1	1.47

The state of aggregation of the particles of such powders, arising from flocculation during precipitation and any slight cementing together during drying, may also be a significant factor affecting use. Comparisons may be made of the relative aggregation of different fillers by use of the electron microscope or by oil-absorption or water-absorption tests [44, 47].

The quoted refractive indices and specific gravities of these commercial products shown in Table XI are all similar and are consistent with the constitution noted. The loose bulk densities, also shown in the table, do not vary widely; they are dependent upon particle size factors more than upon the specific gravity of the material.

VII. Lime-stabilized Soils

The immediate effect of an admixture of lime with soils of high clay content, in reducing the plasticity of the soil, has long been familiar to the farmer. This effect, and a further slow reaction between the lime

and clay causing a ¹ in a compacted lime-road construction and as it is called, is now types of soil, for imprc and sub-bases of roa Africa; Texas and Lo are found (Germany, lime is mixed with an thick. The mixing is g and mix in the lime as or, less commonly, by onto the site (pre clays are believed to in the clay minerals: vironment given by cementation and stres between the lime and lime gradually disapp [49] and that new co components in clays reaction falls within products should be th i.e. they should be h silicates.

Although a great d mechanical and phys published [50, 51], ve Results of only a few they give no more th

This chapter includes Chalk Lime and Allied lished by kind permisic

1. Van Derburgh, G. E.
2. Michaelis, W. (1880)
3. Bessey, G. E. (1948 Rep. No. 3. HMS
4. Nash, G. D., Comrie of Buildings". HI

3. This is com-
ed in the rubber

made up of two
of the particles
al sheet crystal-
5) and granular
ef be a wide
e particle di-

calcium

refractive index	refractive index
—	—
0.05	—
0.1	—
0.1	1.47
0.0	1.45
0.1	1.47
0.0	—
0.1	1.47

ers rising from
g together
use: Comparisons
fillers by use of
absorption tests

s of these com-
d are consistent
lso shown in the
article size factors

soils of high clay
been familiar to
etween the lime

and clay causing a progressive coherence and strength development in a compacted lime-clay mix, are now utilized by the civil engineer in road construction and other works [48]. This soil stabilization by lime, as it is called, is now being widely used with clay, clay-gravel and loess types of soil, for improvement of the sub-grades and construction of bases and sub-bases of roads. Use is most widespread in hot climates (e.g. Africa; Texas and Louisiana, U.S.A.) or where particularly suitable soils are found (Germany, with loess soils). Generally, about 5% by weight of lime is mixed with any layer of soil being stabilized, which may be 4–8 in thick. The mixing is generally done by machines which break up the soil and mix in the lime as they pass over the ground (mix-in-place methods) or, less commonly, by mixing in stationary mixing plant and transporting onto the site (pre-mix methods). The primary changes in plasticity of the clays are believed to be due to physico-chemical effects of base exchange in the clay minerals and of flocculation of the clay in the high pH environment given by the presence of lime. The longer term effect of cementation and strength development is due to a slow chemical reaction between the lime and clay minerals. Chemical tests show that the free lime gradually disappears during moist storage of such lime-clay mixes [49] and that new compounds must therefore be formed. If the minor components in clays (magnesia, iron oxide and alkalis) are ignored, this reaction falls within the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system and the end-products should be the same as for other reacting phases in that system, i.e. they should be hydrous calcium silicates, aluminates and aluminosilicates.

Although a great deal of work on soil stabilization by lime and on the mechanical and physical properties of the stabilized material has been published [50, 51], very little is known so far of the chemistry involved. Results of only a few investigations have been published [52, 53, 54] and they give no more than an indication of the reactions or products.

ACKNOWLEDGMENT

This chapter includes the results of work carried out in the laboratories of The Chalk Lime and Allied Industries Research Association, and is written and published by kind permission of the Council of the Association.

REFERENCES

1. Van Derburgh, G. E. (1886). British Pat. No. 2470.
2. Michaelis, W. (1880). German Pat. No. 14195.
3. Bessey, G. E. (1948). "Sand-Lime Bricks", National Building Studies Spec. Rep. No. 3. HMSO, London.
4. Nash, G. D., Comrie, J. and Broughton, H. F. (1955). "The Thermal Insulation of Buildings". HMSO, London.

5. British Standard Codes of Practice for Building, CP3: Chapter IX, Code of Functional Requirements of Buildings: Durability. British Standards Institution (1950).
6. Poppel, S. V. (1905). Bulletin No. 5, Ohio State Geological Survey, Springfield, Ohio, U.S.A.
7. Parr, S. W. and Ernest, T. R. (1912). Bulletin No. 18, Illinois State Geological Survey, Urbana, Illinois, U.S.A.
8. Gunzelmann, R. (1956). *TonindustrZig* 80, 1.
9. Gvozdev, I. P. (1951). "Proizvodstvo Silikatnogo Kirpicha" ("Manufacture of Sand-lime Bricks"). Promstroizdat, Moscow.
10. The Chalk Lime and Allied Industries Research Association, Welwyn, England. Unpublished report.
11. Jade, K. (1918). *TonindustrZig* 42, 211.
12. Bessey, G. E. and Eldridge, H. J. (1933). *J. Soc. chem. Ind., Lond.* 52, 443T.
13. Wuhner, J., Steyer, W. and Rodermacher, G. (1961). *Zement-Kalk-Gips* 14, 566.
14. Bessey, G. E. and Lea, F. M. (1932). *J. Soc. chem. Ind., Lond.* 51, 91T.
15. Pohl, G. (1957). *Zement-Kalk-Gips* 10, 354.
16. Rinne, F. (1903). *TonindustrZig* 27, 192.
17. Hirsch, H. (1922). *TonindustrZig* 46, 1185.
18. Smirnov, N. N. (1926). *Trans. State Exp. Inst. Silicates (Moscow, U.S.S.R.)* 20, 5.
19. Grime, G. and Bessey, G. E. (1933). *Trans. ceram. Soc.* 32, 14.
20. D.S.I.R. Building Research Station. Annual report, 1938, facing pages 20, 21. HMSO, London.
21. Taylor, H. F. W. (1952). *J. appl. Chem.* 2, 3.
22. Kalousek, G. L. (1954). *J. Amer. Concr. Inst.* 50, 365.
23. Kalousek, G. L. (1955). *J. Amer. Concr. Inst.* 51, 989.
24. Kalousek, G. L. and Prebus, A. F. (1958). *J. Amer. ceram. Soc.* 41, 124.
25. Neese, H., Spangenburg, K. and Weiskirchner, W. (1957). *TonindustrZig* 81, 325.
26. Neese, H. (1959). *TonindustrZig* 83, 124.
27. Aitken, A. and Taylor, H. F. W. (1960). *J. appl. Chem.* 10, 7.
28. Quincke, J. E. (1961). *Bauwirtschaft* 10, 239.
29. Taylor, H. F. W. (1961). "Progress in Ceramic Science", Vol. I, pp. 89-145. Pergamon Press, London.
30. Kalousek, G. L. (1957). *J. Amer. ceram. Soc.* 40, 74.
31. Sanders, L. D. and Smothers, W. J. (1957). *J. Amer. Concr. Inst.* 54, 127.
32. Menzel, C. A. (1934). *J. Amer. Concr. Inst.* 31, 125.
33. Kalousek, G. L. and Adams, M. (1951). *J. Amer. Concr. Inst.* 48, 77.
34. Kalousek, G. L. (1951). U.S. Pat. 2547127.
35. Short, A. and Kinniburgh, W. (1962). "Lightweight Concrete". C.R. Books Ltd., London.
36. Anon. "Silicalcite". Pamphlet issued by Silicalcite, via Calatafimi 7, Padova, Italy.
37. Anon. (1961). *Stroil. Mater.* 7, 29.
38. Huttemann, E. (1961). Private communication.
39. Taylor, W. H. (1954). "Lightweight Concrete." Division of Building Research, C.S.I.R.O. (Australia). Reprinted 1960 with corrections.
40. Moakes, R. C. W. and Pyne, J. R. (1954). *Proc. Inst. Rubb. Ind.* 1, 161.
41. Columbia-Southern
42. Flint, E. P. and Wel
43. Kalousek, G. L. (19
44. Bachmann, J. H., S
45. Chem. Technol. 32
46. Young, G. F. (1958)
47. McDonald, R. S. (11
48. 62, 1168.
49. Dogadkin, B., Pech
50. Moscow 16, 1.
51. American Road B
52. Manual, (Tech. B
53. Clare, K. E. and Cr
54. U.S. Highway
55. Soil Stabilis
56. Brand, W. (1958). S
57. Dumbleton, M. J. (1
58. for Soil Stabilis
59. Tech. Paper No.
60. Andersson, L. H. (11
61. the Swedish Soci
62. Eades, J. L. and C
63. 262, 51.
64. Bessey G. E. New

The author, since v
in the U.S.S.R. the
products mentioned
short note on these
relation thereto, wo
Autoclaved calcin
a very large scale fi
dustrialized bu
buildings, includin
wall units, staircases
According to the pu
forced, and consist
light weight aerated
strength for most ty
but some types ar
or more.

Two main types
involves treatment
speed disintegrator

41. Columbia-Southern Chemical Corp. Silena Bulletin No. 2 (1953).
42. Flint, E. P. and Wells, L. S. (1934). *J. Res. nat. Bur. Stand.* 12, 571. R.P. 687.
43. Kalousek, G. L. (1955). Brit. Pat. 742145; (1957). Brit. Pat. 775582.
44. Bachmann, J. H., Sellers, J. W., Wagner, M. P. and Wolf, R. F. (1959). *Rubb. Chem. Technol.* 32, 1289.
45. Young, G. F. (1958). *J. Colloid Sci.* 13, 67.
46. McDonald, R. S. (1957). *J. Amer. chem. Soc.* 79, 850; (1958). *J. phys. Chem.* 62, 1168.
47. Dogadkin, B., Pechkovskaya, K. and Gol'dman, E. (1957). *Kauchuk i Rezina* Moscow 16, 1.
48. American Road Builders Association. Lime Stabilization Construction Manual. (Tech. Bull. 243 (1959)).
49. Clare, K. E. and Cruchley, A. E. (1957). *Géotechnique* 7, 97.
50. U.S. Highway Research Board Bull. 231 (1959). "Lime and Lime Fly-ash as Soil Stabilisers".
51. Brand, W. (1958). *Strasse u. Autobahn* 9, 426.
52. Dumbleton, M. J. (1962). "Investigations to Assess the Potentialities of Lime for Soil Stabilisation in the United Kingdom." D.S.I.R. Road Research Tech. Paper No. 64. HMSO, London.
53. Andersson, L. H. (1960). "Clay Chemistry in Soil Stabilisation". Reports from the Swedish Society for Clay Research No. 13, 273.
54. Eades, J. L. and Grim, R. E. (1960). U.S. Highway Research Board Bull. 282, 51.
55. Bessey G. E. New data.

ADDENDUM

The author, since writing this chapter, has had opportunity of studying in the U.S.S.R. the wider developments in the use of calcium silicate products mentioned briefly on p. 126. It is possible to add here only a short note on these developments which, with research carried out in relation thereto, would merit additional chapters in this book.

Autoclaved calcium silicate processes are now used in the U.S.S.R. on a very large scale for production of all types of building units for industrialized building techniques. Indeed the entire structures of some buildings, including floor and roof units, large external and internal wall units, staircases, beams, pillars and lintels, consist of these materials. According to the purpose being served, the units may be plain or reinforced, and consist of high or medium strength, dense ($D = 1.8-2.2$) or light weight aerated ($D = 0.7-0.8$) material. The minimum compressive strength for most types of unit in the dense materials is about 3000 lb/in² but some types are being produced with strengths of 10,000 lb/in² or more.

Two main types of process are: used the "Silicalcit" process which involves treatment of the whole of the sand and lime mixture in a high speed disintegrator which is said to produce highly reactive surfaces on